

EFFECTS OF SOLVENT AND CATALYST ON LIQUEFACTION CONVERSION AND STRUCTURAL CHANGES OF A TEXAS SUBBITUMINOUS COAL

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INTRODUCTION

Coal liquefaction involves an initial stage of coal macromolecular break-up driven by thermal energy [1, 2]. The result of this break-up is the formation of free radicals. If these free radicals are stabilized by hydrogenation, a liquid product is formed and the goal of liquefaction is achieved. On the contrary, if the radicals recombine with one another and form more stable and heavier product, the liquefaction has failed. Therefore, hydrogenation is the key in coal liquefaction. In fact, a recent study showed that the more hydrogen consumed in the reaction, the higher conversion would be obtained [3]. There are several ways often used to accelerate the rate of hydrogenation: to use a high pressure of H_2 [4], to use a hydrogen-donor solvent [5], and to use a catalyst.

In this study, a Big Brown Texas subbituminous (DECS-1) coal was used for liquefaction. A low-rank coal like this is characterized by low aromaticity, small ring clusters, abundant aliphatic and hydroaromatic carbon, and high oxygen content [6]. These structural features cause the thermal break-up of the coal over a wide temperature range [7-9], and thus the hydrogenation should be feasible in the same range. The purpose of this work is to investigate the liquefaction of DECS-1 at temperature range from 250°C to 450°C. Two kinds of solvent, a hydrogen-donor solvent (tetralin) and a non-donor solvent (1-methylnaphthalene) were used to compare with the reactions without solvent. An ammonium-tetrathiomolybdate-derived catalyst was used. Liquefaction results are presented to determine the solvent effect and the catalyst effect. The residues from tetrahydrofuran (THF) extraction of the reaction products were studied by CPMAS ^{13}C NMR to obtain their aromaticities. Furthermore, the conversion and the aromaticity data were combined to calculate the amount of aliphatic and aromatic carbon that has reacted and has been removed from the coal during liquefaction.

EXPERIMENTAL

The coal sample was a Big Brown Texas subbituminous (DECS-1) obtained from the Penn State Coal Sample Bank. Its compositional data are summarized as the following on a dry and mineral matter free basis: 76.13% carbon, 5.54% hydrogen, 1.50% nitrogen, 1.05% organic sulfur and 15.78% oxygen (by difference). The reaction solvents were tetralin (Aldrich, 99%), and 1-methylnaphthalene (1-MN, Aldrich, 98%). The catalyst precursor was ammonium tetrathiomolybdate (ATTM, Aldrich, 99.97%). All the chemicals were used without further purification.

The catalyst loading was 1 wt% of Mo based on the dmmf coal. A THF/ H_2O (1:1) mixture was used to make the solution of the catalyst precursor, because this binary mixture was superior to H_2O in terms of providing higher conversion and oil yield in subsequent liquefaction [10]. The catalyst precursor was first added to water, of just enough volume to dissolve the desired amount of the precursor. An equal volume of THF was then added to the H_2O solution. After being stirred to achieve a homogeneous mixture, the THF/ H_2O /ATTM mixture was added to the dried coal to make a slurry. After 20 minutes of stirring at room temperature under N_2 atmosphere, the excess water and THF was removed by rotary evaporator. The "wet" sample (still containing some residual H_2O and THF) was then dried in a vacuum oven at room temperature for 20 hours, at 45°C for 5 hours and at 95°C for 4 hours, sequentially.

Liquefaction experiments were conducted in 25 ml microautoclaves in a fluidized sandbath. For each reaction, 4 grams of the coal sample and 4 grams of a solvent, if a solvent was applied, were loaded into a microautoclave. The reactor was purged three times with hydrogen and the final H₂ pressure was 1000 psi (7 MPa) at room temperature. For every reaction, the sandbath was preheated to a desired temperature, 250°C, 300°C, 350°C, 400°C, or 450°C. The microautoclave was then plunged into the sandbath and agitated at a rate of 200 cycles per minute. The total time in which a microautoclave was kept in the sandbath was 33 minutes, with 3 minutes being the time for rapid heat up. Finally, after reaction, the microautoclave was taken out of the sandbath and rapidly quenched by dipping into cold water.

After the microautoclave was cooled to room temperature, the reactor was vented, the volume of the gas was measured by the water displacement method, and a sample was collected for further analysis. The liquids and the solids in the microautoclave were washed into a tared ceramic thimble using hexane. Then the products were separated under a nitrogen atmosphere by Soxhlet extraction using hexane, toluene and THF sequentially. The soluble products are classified as oil, asphaltene and preasphaltene, respectively.

The THF insolubles were analyzed by ¹³C solid state NMR using cross polarization magic angle spinning (CPMAS) technique. All CPMAS spectra were obtained on a Chemagnetics NMR Model M100s. The ¹³C frequency was 25.15 MHz. The pulse delay was 1 second and the contact time was 1 ms.

RESULTS AND DISCUSSION

The results of liquefaction without catalyst are listed in Table 1. Conversions are in a large range, from 11.7% to 92.2%. At 250°C, the solvents do not show any significant effect on conversion or product distribution. As the temperature increases to 300°C, the solvents start showing their advantage by providing slightly higher conversions than the reaction without solvent. At 350°C, there is a remarkable increase in oil, asphaltene and preasphaltene yields when a solvent is used. This indicates that in this temperature range, the solvents play a role which enhances the conversion, but since there is no difference between the reaction with tetralin and the reaction with 1-MN, this role may not relate to hydrogen donation. In the temperature range from 350°C to 400°C, there is a drastic increase in conversion no matter whether a solvent is applied or not, suggesting that at this temperature range, thermal energy is enough to break down the coal macromolecular matrix. At 400°C, tetralin made a tremendous difference from 1-MN and no solvent. The conversion reaches 82.0%, composed of gas, 9.5%; oil, 36.7%; asphaltene, 16.6%; and preasphaltene, 19.2%. With 1-MN or without solvent, the conversions are much less, 55.5% and 45.0% respectively. The differences of conversion and product distribution imply that tetralin is active in donating hydrogen at temperatures higher than 350°C. 1-MN, on the other hand, shows a very slight advantage over no solvent in gaining higher conversion and oil yield, but as temperature increases to 450°C, this advantage almost disappears.

The results of catalytic liquefaction are presented in Table 2. In the presence of ATTm, the conversion of all experiments increase drastically as the temperature increases from 250°C to 400°C. Comparing the reactions with no solvent, tetralin or 1-MN with the corresponding non-catalytic reactions, the catalyst increased the conversion, especially at temperatures higher than 300°C, suggesting that ATTm was converted to an active catalyst at temperature between 300°C and 350°C [11]. Furthermore, the product distribution shows that the increasing conversion is accompanied by an increasing yield of light materials, such as oil, when the catalyst is added. The other comparison is among the three kinds of catalytic reactions. At temperatures between 250°C and 400°C, there is no significant difference in conversion and product distribution (though at 400°C the reaction without solvent seems to have higher oil yield). In this temperature range, the catalyst has a stronger effect than the solvents; thus any difference caused by the solvents is diminished. However, at 450°C, tetralin gave a slightly higher conversion while both 1-MN and no solvent actually gave a much lower conversion (almost 20 percentage units lower) relative to those at 400°C. In the case of 1-MN at

450°C, the yields of gas, asphaltene and preasphaltene are still very similar to those in tetralin, while the conversion is much lower. The sole cause of this conversion difference is the decrease of the oil yield. With tetralin at 450°C, yields of asphaltene and preasphaltene dropped by 9 percentage units and 17 percentage units respectively, while the yield of oil increased by 22 percentage units compared with that at 400°C. This suggests that at this temperature (450°C), in the presence of both catalyst and a H-donor solvent, the conversion from preasphaltene and asphaltene to oil, or from heavy products to light products, is favorable. With the presence of the catalyst but absence of a donor solvent (meaning with no solvent or a non-donor solvent), the conversion drops as well as all of the product yields, except gas, suggesting that retrogressive reactions take place and form heavier and more stable materials.

In coal liquefaction, once the free radicals are formed, the reactions that they undergo are the result of a competition between radical stabilization by hydrogenation to form light products and recombination of the radicals to form heavy products. Since the free radical formation is a pyrolytic break-up of coal matrix, it is a thermally driven reaction [1]. At low temperatures (up to 400°C), the rate of radical formation is so slow that the hydrogenation rate can catch up, regardless of whether the hydrogen radicals are from the donor solvent or from the gaseous H₂. However, at 450°C, radical formation from the coal is very fast, but the H radical from catalytic decomposition of gaseous H₂ is not as fast, and therefore radical recombination is more likely to take place. Since tetralin has intimate contact with these radicals and is able to donate H, hydrogenation can still take place to form light products.

The gas yields from all liquefaction experiments are plotted versus temperature in Figure 1. All the yields are in the range from 0% to 20%. Regardless of the solvents and the catalyst used in the reactions, they all fall on one line. Therefore, the amount of gas produced in the reactions is a function only of temperature. Since neither a solvent nor a catalyst has any effect, gas formation is a reaction driven by thermal energy.

Examples of the spectra of CPMAS ¹³C NMR of residues are shown in Figure 2. The spectra were curve-fitted using LabCalc program and the area of each peak was integrated. The aromaticities of the raw coal and the dried coal are both 0.48. This shows that before reaction, the aromaticity is not affected by vacuum drying at 95°C. The aromaticities of residues from all runs are summarized in Table 3. It is observed that as temperature increases, the aromaticity increases from 0.50 to 0.94. There are two possible explanations of this increase: one is that as reaction temperature increases, more and more aliphatic carbons are cracked from the macrostructure of the coal while the aromatic carbon may not react as much; the other is that dehydrogenation and condensation reactions take place during the reaction increasing the amount of aromatics in the coal. Comparing the aromaticities of the residues from the non-catalytic reactions, it is found that the solvents do not have a significant effect. Furthermore, in the case of catalytic reactions, the solvents have no significant effect either. In order to determine the influence of the catalyst on the aromaticities, all the data are plotted versus conversion in Figure 3. A general trend is that the aromaticities of residues increase with conversion, but the data fall into two separate sets: those from reactions with and without the catalyst, regardless of the solvent used. Generally, *f_a* of the residue from a catalytic reaction is lower than that from a non-catalytic reaction, and the difference between the two increases with increasing conversion. At the most severe conditions, 450°C with the catalyst, the aromaticities deviate from the line of catalytic reaction. The higher aromaticities are caused by more aromatic carbon, which indicates the retrogressive reactions at this temperature. In non-catalytic reactions, the use of tetralin at 400°C and 450°C results in lower aromaticities, suggesting that tetralin helps to convert aromatic carbons from coal to THF solubles.

To achieve a general idea on what kinds of structure have been converted to THF solubles, or what kinds of reactions are actually catalyzed by the catalyst during the liquefaction, the percentages of aliphatic and aromatic carbon that have been reacted are calculated from the amounts of dry, mineral-matter-free coal charged, aromaticity of the dried coal, the conversions, and the aromaticities of the residues. In Figure 4, the extent of reacted aliphatic carbon is shown as a function of temperature. At each temperature, the lowest point always corresponds to the reactions with no

solvent and no catalyst. As expected, these reactions with the worst liquefaction conditions result in the lowest conversion of aliphatic carbon. Comparing the effects of the solvents, the catalyst and temperature, the latter is shown to be the most significant by the fact that highest conversion of aliphatic carbon at one temperature is always lower than the lowest conversion at the next temperature (except that between 400°C and 450°C). Roughly speaking, all the points stay on one curve, regardless of the use of solvent or catalyst. The amount of reacted aliphatic carbon increases nearly linearly when the temperature increases, up to 400°C. At 400°C, about 90% of the aliphatic carbon has been converted to THF solubles. When the reaction temperature was further increased to 450°C, the increase of the reacted aliphatic carbon became insignificant, from 90% to about 95%. This study suggests that, like the yields of the gases, the conversion of aliphatic carbon from coal to THF solubles is a function mainly of temperature, neither solvent nor catalyst has any influence on it. In Figure 5, the amount of aromatic carbon converted to THF solubles is plotted versus the temperature. Unlike those in Figure 4, the data are much more scattered in Figure 5. In non-catalytic liquefaction reactions, tetralin made a remarkable difference from 1-MN and no solvent. When the temperature was 350°C or higher, much more of the aromatic carbon reacted in the presence of tetralin. At 450°C, the conversion of aromatics reached 86% with tetralin, while it only reached 15% and 10% with 1-MN and without solvent respectively. In catalytic liquefaction reactions, the difference caused by the solvents is diminished when the temperature increases to 400°C, indicating that the catalyst is sufficiently active in converting the aromatics into THF solubles and that solvent is no longer a major determining factor. However, when the temperature increased to 450°C, with the presence of the catalyst, reactions with 1-MN or without a solvent have a large decrease from 77% to 36% and from 93% to 42% respectively, while that with tetralin increased from 87% to 92%. At temperature as high as 450°C, the thermal cracking of the coal matrix is very fast, and the hydrogenation from the gaseous H₂ catalyzed by the added catalyst is no longer able to catch up. Therefore at 450°C in the presence of the catalyst, tetralin is no longer a minor factor. In fact, the only way to prevent the retrogressive reaction is to have a donor solvent, such as tetralin.

The study of reacted aliphatic and aromatic carbon helps to explain why a non-catalytic reaction always produces residues with higher aromaticity than a catalytic reaction even though the conversion can be the same. In the former case, the conversion is achieved by having more aliphatic carbon reacted and in the latter case, it is achieved by having a greater proportion of aromatic carbon reacted. For example, in experiment no. 331, the conversion is 44.0%, there is -8% aromatic (i. e. implying retrogressive aromatization reactions) and 79% aliphatic carbon reacted; while in experiment no. 327, the conversion is 45%, there are 23% aromatic and 63% aliphatic carbon reacted.

SUMMARY

Liquefaction of a Big Brown Texas subbituminous coal was studied in the temperature range from 250°C to 450°C. Tetralin and 1-MN were used as reaction solvents to compare with the reactions without solvent. Ammonium tetrathiomolybdate was used as the catalyst precursor. In thermal experiments, tetralin, a H-donor solvent, was beneficial not only in gaining high conversion but, most importantly, also in gaining high yield of oil at temperatures higher than 350°C. In catalytic experiments, conversions are very similar regardless of solvent used at temperatures up to 400°C, and tetralin does not have an advantage. However, at 450°C, conversions with 1-MN or with no solvent dropped while that with tetralin increased, as well as the oil yield. The gas yields appears to be independent of solvent and catalyst but dependent on temperature.

Cross polarization magic angle spinning of ¹³C NMR was performed to obtain aromaticities of reaction residues. It is found that in the plot of aromaticity versus conversion, the data fall into two sets: the non-catalytic reactions and the catalytic reactions. With the same conversion, a residue from a catalytic reaction always has lower aromaticity. This is because in a catalytic reaction, more aromatic carbon has been reacted. The study of the amount of aliphatic carbon converted from the coal to THF solubles shows that neither the catalyst nor the solvents has influence on it, but it is a function of temperature. In the case of conversion of aromatic carbon from coal to THF solubles, both the catalyst and the solvents have strong effects. For non-catalytic reactions, tetralin gave much

higher conversions of aromatic carbon than 1-MN or no solvent. For catalytic reactions, there is no difference among the solvents (or no solvent) at temperatures up to 400°C. At temperatures higher than 400°C, tetralin again gave a much higher conversion than the other two cases, indicating that the hydrogen donation by the solvent played a significant role. As for 1-MN and no solvent, compared with the results at 400°C, the conversion of aromatic carbon at 450°C did not increase, in fact it decreased drastically, suggesting that retrogressive reactions occur in these situations.

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Table 1. Conversion and yield of non-catalytic reactions

| Expt.# | Description | Conv. | Gas | Oil | Asph. | Preasph. |
|--------|--------------|-------|------|------|-------|----------|
| 317 | 250C, NC, NS | 11.7 | 1.9 | 8.2 | 0.8 | 0.8 |
| 318 | 250C, NC, TE | 13.3 | 0.6 | 6.0 | 3.7 | 3.1 |
| 319 | 250C, NC, MN | 11.9 | 2.8 | 5.6 | 2.4 | 1.2 |
| 335 | 300C, NC, NS | 16.2 | 3.5 | 7.9 | 0.9 | 3.9 |
| 336 | 300C, NC, TE | 20.8 | 3.5 | 9.8 | 3.5 | 4.0 |
| 337 | 300C, NC, MN | 22.2 | 3.5 | 10.2 | 2.0 | 6.5 |
| 320 | 350C, NC, NS | 19.1 | 6.5 | 7.4 | 1.2 | 4.1 |
| 307 | 350C, NC, TE | 38.2 | 4.4 | 18.2 | 8.3 | 7.4 |
| 309 | 350C, NC, MN | 33.8 | 5.0 | 14.8 | 7.4 | 6.7 |
| 331 | 400C, NC, NS | 45.0 | 11.6 | 19.8 | 3.4 | 10.2 |
| 332 | 400C, NC, TE | 82.0 | 9.5 | 36.7 | 16.6 | 19.2 |
| 334 | 400C, NC, MN | 55.5 | 9.7 | 24.4 | 10.4 | 11.0 |
| 349 | 450C, NC, NS | 51.5 | 17.6 | 28.8 | 0.9 | 4.2 |
| 350 | 450C, NC, TE | 92.2 | 19.2 | 49.0 | 8.4 | 15.6 |
| 351 | 450C, NC, MN | 57.0 | 16.3 | 31.8 | 4.3 | 4.6 |

Table 2. Conversion and yield of catalytic reactions

| Expt. # | Description | Conv. | Gas | Oil | Asph. | Preasph. |
|---------|----------------|-------|------|------|-------|----------|
| 322 | 250C, ATTM, NS | 5.0 | 0.9 | 0.0 | 3.1 | 3.8 |
| 323 | 250C, ATTM, TE | 3.8 | 0.9 | 0.0 | 2.3 | 1.7 |
| 324 | 250C, ATTM, MN | 3.6 | 0.6 | 6.0 | 2.3 | 2.5 |
| 338 | 300C, ATTM, NS | 17.2 | 2.5 | 9.3 | 1.8 | 3.6 |
| 339 | 300C, ATTM, TE | 22.0 | 0.9 | 12.4 | 5.5 | 3.2 |
| 340 | 300C, ATTM, MN | 22.9 | 2.4 | 10.2 | 6.0 | 4.3 |
| 325 | 350C, ATTM, NS | 39.4 | 4.0 | 23.2 | 6.2 | 6.0 |
| 326 | 350C, ATTM, TE | 46.6 | 3.7 | 23.9 | 11.4 | 7.6 |
| 327 | 350C, ATTM, MN | 44.0 | 3.4 | 18.5 | 9.9 | 12.2 |
| 328 | 400C, ATTM, NS | 95.5 | 7.4 | 58.9 | 24.0 | 5.2 |
| 329 | 400C, ATTM, TE | 92.0 | 6.8 | 44.3 | 19.3 | 21.6 |
| 330 | 400C, ATTM, MN | 84.8 | 8.1 | 41.6 | 16.4 | 18.7 |
| 352 | 450C, ATTM, NS | 69.4 | 18.0 | 44.6 | 5.2 | 1.6 |
| 353 | 450C, ATTM, TE | 95.8 | 14.2 | 66.1 | 10.4 | 5.1 |
| 354 | 450C, ATTM, MN | 67.2 | 16.1 | 37.4 | 8.4 | 5.3 |

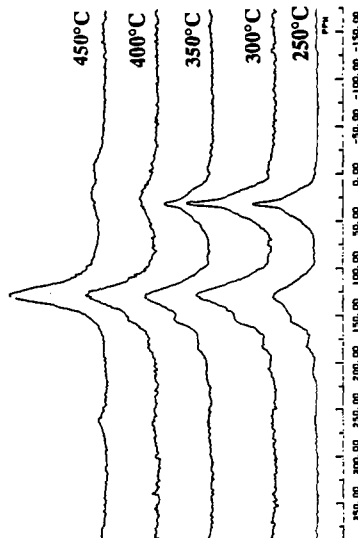


Figure 2. NMR spectra of residues from non-catalytic reactions with tetralin

Table 3. Aromaticity of residues from all liquefaction experiments

| T (°C) | nc/ns | nc/tetr. | nc/l-mn | atm/ns | atm/tetr. | atm/l-mn |
|--------|-------|----------|---------|--------|-----------|----------|
| 250.0 | 0.52 | 0.50 | 0.53 | 0.50 | 0.52 | 0.52 |
| 300.0 | 0.55 | 0.63 | 0.60 | 0.45 | 0.57 | 0.58 |
| 350.0 | 0.64 | 0.69 | 0.74 | 0.59 | 0.62 | 0.66 |
| 400.0 | 0.80 | 0.85 | 0.86 | 0.78 | 0.76 | 0.72 |
| 450.0 | 0.89 | 0.91 | 0.94 | 0.85 | 0.94 | 0.93 |

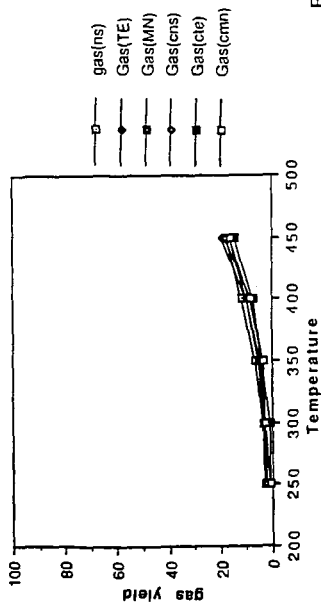


Figure 1. Gas yield of all liquefaction experiments

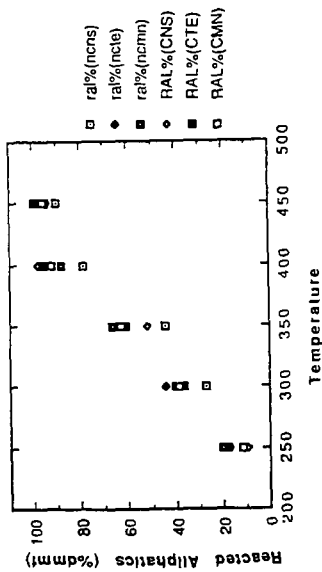


Figure 4. Reacted aliphatic carbon as a function of temperature

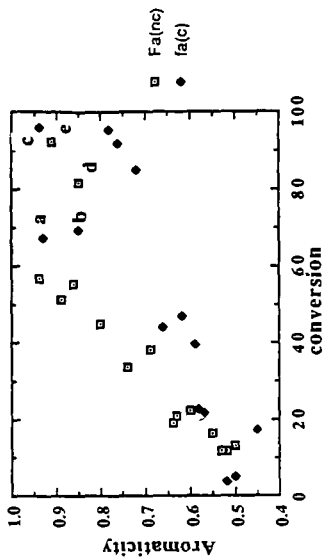


Figure 3. Aromaticity of residues from all experiments as a function of conversion a, b, c, aromaticities of catalytic reaction at 450°C with 1-MN, no solvent and tetralin respectively; d, e, aromaticities of residue from non-catalytic reactions with tetralin at 400°C and 450°C.

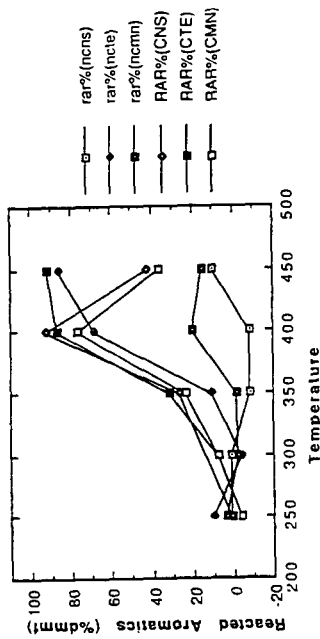


Figure 5. Reacted aromatic carbon as a function of temperature